

NbFe_{1.28}Te₃, a quasi-layered ternary niobium telluride compound

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Abstract

NbFe_{1.28}Te₃, a new ternary niobium telluride compound, was synthesized via solid state reactions. The crystal structure of this compound was determined by single crystal X-ray diffraction methods. The structure belongs to the monoclinic space group $P2_1/m$ (number 11) and is isostructural with TaFe_{1.25}Te₃. The following cell constants were obtained from the analysis: $a=7.373$ Å, $b=3.648$ Å, $c=9.965$ Å, $\beta=108.81^\circ$, $Z=2$. The final refinement yielded $R=3.5\%$ and $R_w=4.6\%$. The structure can be described as a quasi-two-dimensional layered type. It consists of an Nb–Fe1–Nb metal network “sandwiched” by the Te and Fe2 atoms from above and below. This would result in an “NbFe₂Te₃” layer if the Fe2 sites were fully occupied. Connections between the layers are made through Fe2–Te2 bonds. The Fe2 atoms reside in square pyramidal sites and are bonded to four basal Te atoms from one layer and an apical Te2 atom from the adjacent layer. The partial occupancy of the Fe2 sites leads to a non-stoichiometric formula NbFe_{1.28}Te₃. The metal–metal bonding in this structure is quite unusual.

1. Introduction

Transition metal chalcogenides show great potential for important technological applications. Most of the binary systems form low-dimensional structures of chain or layered type. They have been studied extensively due to many unusual and interesting properties, such as superconductivity, charge-density waves, ferromagnetism and anti-ferromagnetism, phase transitions and anisotropic electrical and optical behavior [1]. These materials have been used as reversible battery electrodes, high-temperature lubricants, solid state lasers, synthetic conductors and heterogeneous catalysts [2]. In addition, some have shown very rich intercalation chemistry [3]. In the last few years, interest in the ternary group V chalcogenide compounds has also grown. As a result, a considerable number of these phases have been synthesized and studied [4]. Many are metal rich with unusual structural features. During our search for novel low-dimensional ternary telluride materials, we have worked closely with the niobium and tantalum telluride derivatives, and have successfully crystallized and characterized several compounds in this category [5]. In this paper, we report the synthesis and structure of NbFe_{1.28}Te₃, a quasi-two-dimensional ternary niobium telluride compound.

2. Synthesis

Single crystals of NbFe_{1.28}Te₃ were obtained from chemical transport reactions at 700–750 °C with TeCl₄ as transport agent. A 1 g mixture of the elements Nb (99.98%, Strem Chemicals, Inc., Newburyport, MA), Fe (99.999%, AESAR/Johnson Matthey, Ward Hill, MA) and Te (99.999%, Aldrich Chemical Company, Milwaukee, WI) with a molar ratio of Nb:Fe:Te = 4:5:12 was weighed and transferred to a quartz tube (length, 6 in; internal diameter, 10 mm). TeCl₄ (10 mg) was added to the mixture and the tube was evacuated and sealed with a torch. The reaction was then heated to 750 °C within 9 h and kept at this temperature for 10 days. After being cooled slowly to room temperature, the container was removed from the furnace. Well-formed long, needle-like crystals were found mostly at the cool end of the reaction tube. These crystals show metallic luster and are stable in air. Reactions of the same starting materials at higher temperatures also produced a second phase, Nb₄FeTe₄ [4d].

3. Structure determination

Microprobe analysis of the crystals on a Jeol JXA-8600 Superprobe indicated the presence of all three elements (Nb:Fe:Te = 1:1.14:2.57). The NbFe_{1.28}Te₃ structure was solved by single crystal X-ray diffraction.

TABLE 1. Crystal data and cell constants of NbFe_{1.28}Te₃

Chemical formula	NbFe _{1.28} Te ₃	Density (calculated)	7.156 g cm ⁻³
Space group	<i>P</i> 2 ₁ / <i>m</i> (11)	λ	0.71069 Å
<i>a</i>	7.373(1) Å	Absorption coefficient μ	232 cm ⁻¹
<i>b</i>	3.648(1) Å	θ range	2–35°
<i>c</i>	9.965(2) Å	Largest and mean Δ/σ	0.002/0.001
α, β, γ	90°, 108.81(1)°, 90°	Observed reflections	1077 ($I > 2\sigma(I)$)
Formula weight	273.6 g mol ⁻¹	R^a	3.5%
<i>V</i>	253.7(1) Å ³	R_w^b	4.6%
<i>Z</i>	2	Goodness of fit (GOF)	1.253

$$^aR = \sum(|F_o| - |F_c|) / \sum(|F_o|)$$

$$^bR_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}, w = 1/(\sigma^2(F) + 0.0009F^2)$$

The crystal used in the analysis had dimensions of 0.34 mm × 0.01 mm × 0.03 mm. Data collection was carried out on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Unit cell constants were obtained from refinement on 25 accurately centered reflections ($\theta = 15$ –20°). Two octants of data ($0 < h < 11, 0 < k < 5, -15 < l < 15$) were collected and merged. Three standard reflections, measured every 2 h during the data collection, showed no intensity decay. Systematic absences were consistent with only a 2₁ axis, and the ($E^2 - 1$) statistics (SHELXS) indicated a centrosymmetric space group *P*2₁/*m*. The analytical absorption correction was based on a gaussian grid method, using bounding faces (1 0 0), (-1 0 0), (1 -1 1), (-1 1 -1), (1 0 -2) and (-1 0 2). A total of 1197 unique reflections with $I > 2\sigma(I)$ were used in the structure refinement. An isotropic extinction correction, $\eta = 0.0022(3) \times 10^{-4}$, was applied to the data and refined. The refinement yielded $R = 3.5\%$, $R_w = 4.6\%$ and a goodness of fit (GOF) of 1.25*. The partially occupied Fe2 site was refined with a high degree of precision to give the formula NbFe_{1+x}Te₃, $x = 0.28(2)$. Detailed crystal data and unit cell constants are listed in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are given in Table 2.

TABLE 2. Atomic coordinates and equivalent isotropic displacement coefficients for NbFe_{1.28}Te₃

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ($\times 10^4$ Å ²)
Nb	2e	0.83487(9)	0.2500	0.30206(7)	102(3)
Fe1	2e	0.61250(15)	0.7500	0.08720(11)	106(4)
Fe2	2e	0.76884(56)	0.2500	-0.00624(41)	117(18)
Te1	2e	0.43859(7)	0.2500	0.18883(5)	112(2)
Te2	2e	0.98463(7)	0.7500	0.15910(5)	108(2)
Te3	2e	0.22071(7)	0.2500	0.49600(5)	103(2)

$$U(\text{eq}) = 1/3(U_{11} + U_{22} + U_{33})$$

*The goodness of fit (GOF) is given by $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$, where NO is the number of observations and NV is the number of variables.

4. Results and discussion

Strictly speaking, NbFe_{1.28}Te₃ is a three-dimensional solid constructed from layers of an “NbFe₂Te₃” network. It is isostructural with the previously reported TaFe_{1.25}Te₃ [5d]. The Nb–Fe1–Fe1–Nb metallic units (Nb–Fe1 = 2.888 Å), capped by Te and Fe2 atoms on both sides, are stacked along the crystallographic *b* axis to form an infinite ribbon-like structure. These “ribbons” are bridged by Te3 atoms through Nb–Te3 bonds (Nb–Te3 = 2.842 Å × 2, 2.879 Å) to give rise to an “NbFe₂Te₃” layer. Connections between the layers are made solely by single bonds between the Fe2 and Te2 atoms from the adjacent layers (2.723 Å) which are longer than the Fe2–Te2 bonds within the ribbon (2.624 Å). There are only two such bonds per unit cell, resulting in large empty channels running parallel to the crystallographic *b* axis (see Fig. 1). For this reason, the structure may be alternatively considered as quasi-two-dimensional. The Nb atom is nine coordinate. Six Te atoms form a distorted octahedron around the Nb (Nb–Te1 = 2.773 Å, Nb–Te2 = 2.756 Å × 2, Nb–Te3 = 2.842 Å × 2, 2.879 Å). The average Nb–Te distances are comparable with those found in NbTe₂ [6]. Nb also

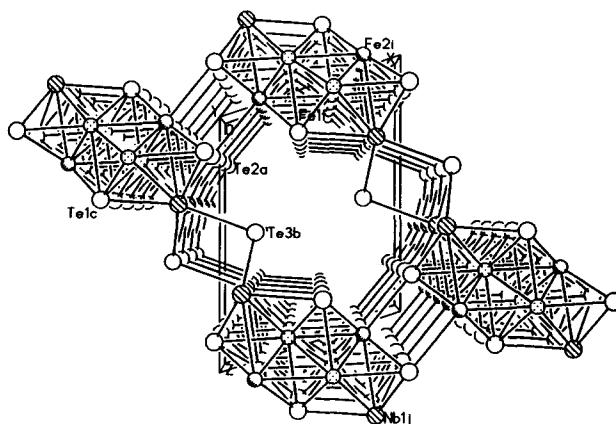


Fig. 1. Perspective view of the NbFe_{1.28}Te₃ structure along the crystallographic *b* axis: ○, Te atoms; ●, Fe1 atoms; ●, Fe2 sites; ●, Nb atoms.

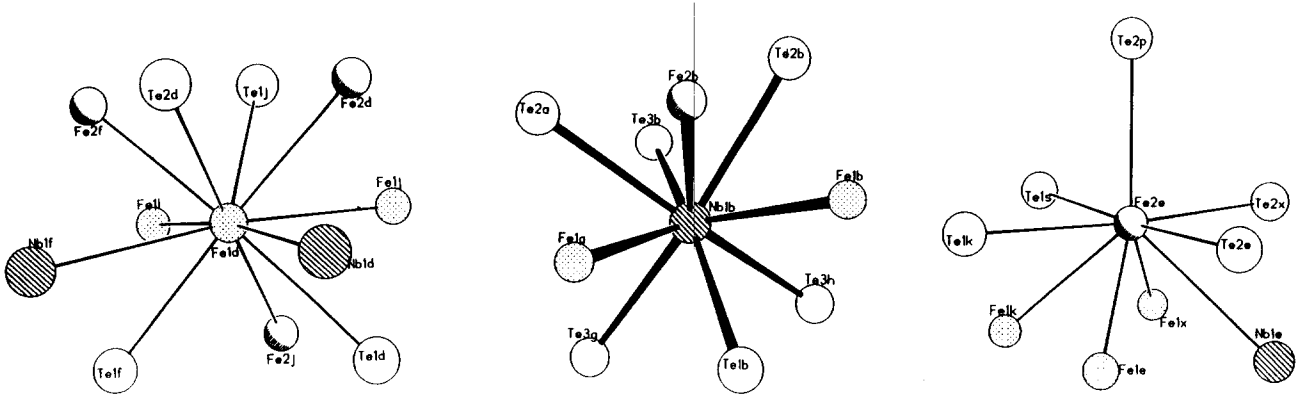


Fig. 2. Views showing the atomic coordinates for Nb, Fe1 and Fe2 atoms. To simplify the picture, only those bonds to the central atom are drawn. The symbols are the same as in Fig. 1.

forms two bonds with Fe1 and one with Fe2 atoms (Nb–Fe2=2.952 Å). The Fe1 atom has a higher coordination number (eleven). It is bonded to four Te atoms in a distorted tetrahedral geometry (Fe1–Te1=2.615 Å×2, 2.654 Å, Fe1–Te2=2.604 Å), to two Nb and two Fe1 atoms which form a distorted rectangle (Fe1–Fe1=2.691 Å×2) and to three Fe2 atoms (Fe1–Fe2=2.494 Å×2, 2.665 Å). The octahedral coordination of Nb (or Ta) atoms and the tetrahedral coordination of Fe atoms have been found in a number of ternary telluride compounds [4a, 4b, 4f, 5a–5d]. The Fe2 sites are partially occupied, giving rise to the non-stoichiometric formula NbFe₁Fe₂_xTe₃ ($x=0.28$). Each Fe2 atom has nine bonds: one to the Nb atom, three to Fe1 atoms and five to Te atoms that form a distorted square pyramid (Fe2–Te1=2.681 Å×2, Fe2–Te2=2.624 Å×2, 2.723 Å). Such Fe-to-Te coordination is quite unusual. The atomic coordination of the Nb and Fe atoms is drawn in Fig. 2. Selected bond lengths and bond angles are listed in Table 3. A careful comparison of the two isostructural phases shows that all Fe–Te distances in NbFe_{1.28}Te₃ are slightly longer than those in TaFe_{1.25}Te₃, except Fe2–Te2, the bond that connects the two adjacent layers, which is 0.043 Å shorter. In addition, the Nb–Fe bonds are slightly longer than the corresponding Ta–Fe bonds. The shortest interlayer Te–Te contact, on the other hand, is almost 0.1 Å shorter in NbFe_{1.28}Te₃ (3.648 Å *vs.* 3.741 Å in TaFe_{1.25}Te₃).

Strong metal–metal interactions are present in the NbFe_{1.28}Te₃ structure. These are reflected in Table 3, where all metal–metal bonds are listed. Although somewhat longer than the sum of the covalent radii of the two elements (2.51 Å for Nb–Fe, 2.31 Å for Fe–Fe), they certainly represent covalent-type bonding. Metal networks are a common feature in many ternary telluride compounds, as found in, for example, Ta₄SiTe₄ [4d], TaM₂Te₂ [4j], M'MTe₂ (M'≡Nb, Ta; M≡Fe, Co, Ni) [5a, 5e] and the isostructural TaFe_{1.25}Te₃ [5d].

TABLE 3. Selected bond distances and angles for NbFe_{1.28}Te₃

Bond	Distance (Å)	Bond	Angle (°)
Nb–Fe1	2.888(1)×2	Fe2–Nb–Fe1	50.5(1)
Nb–Fe2	2.952(4)	Te1–Nb–Fe1	55.0(1)
Nb–Te1	2.773(1)	Te1–Nb–Fe2	77.2(1)
Nb–Te2	2.756(1)×2	Te2–Nb–Te1	109.6(1)
Nb–Te3	2.842(1)×2	Te3–Nb–Fe1	134.4(1)
Nb–Te3	2.879(1)	Te3–Nb–Te1	163.2(1)
Fe1–Fe1	2.691(2)×2	Te3–Nb–Te2	82.7(1)
Fe1–Fe2	2.494(3)×2	Fe2–Fe1–Nb	66.1(1)
Fe1–Fe2	2.665(3)	Te1–Fe1–Nb	60.3(1)
Fe1–Te1	2.615(1)×2	Te1–Fe1–Fe2	88.7(1)
Fe1–Te1	2.654(1)	Te2–Fe1–Nb	60.0(1)
Fe1–Te2	2.604(1)	Te2–Fe1–Fe2	61.9(1)
Fe2–Te1	2.681(3)×2	Te2–Fe1–Te1	119.9(1)
Fe2–Te2	2.624(3)×2	Fe2'–Fe1–Te2	178.4(1)
Fe2–Te2	2.723(3)	Fe1–Fe2–Nb	63.4(1)
Te2–Te2	3.648(1) (interlayer, shortest)	Te2–Fe2–Nb	58.9(1)
		Te2–Fe2–Fe1	61.1(1)
		Te2'–Fe2–Te1'	87.6(1)

The Te atoms in this compound cannot be described in terms of simple close-packed layers [5d]. The shortest interlayer Te–Te contact, 3.648 Å, is between the two Te2 atoms and is typical of layered telluride compounds.

Temperature-dependent electrical conductivity and magnetic susceptibility studies of TaFe_{1.25}Te₃ have revealed some interesting behavior. Investigations of the physical and electronic properties of NbFe_{1.28}Te₃ are currently being carried out in our laboratory. We will discuss the results in a separate report.

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